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(21) International Application Number: PCT/US97/08544 (22) International Filing Date: 16 May 1997 (16.05.97) (30) Priority Data: <table border="0"><tr><td>60/017,884</td><td>17 May 1996 (17.05.96)</td><td>US</td></tr><tr><td>60/017,883</td><td>17 May 1996 (17.05.96)</td><td>US</td></tr><tr><td>60/017,886</td><td>17 May 1996 (17.05.96)</td><td>US</td></tr><tr><td>9616076.6</td><td>31 July 1996 (31.07.96)</td><td>GB</td></tr><tr><td>9705824.2</td><td>20 March 1997 (20.03.97)</td><td>GB</td></tr></table> (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ASKEW, Stuart, Clive [GB/GB]; 17 Mayfair Road, West Jesmond, Newcastle upon Tyne NE2 3DN (GB). SORRIE, Graham, Alexander [GB/GB]; 14 Curlew Hill, Lancaster Park, Morpeth, Northumberland NE61 3SH (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		60/017,884	17 May 1996 (17.05.96)	US	60/017,883	17 May 1996 (17.05.96)	US	60/017,886	17 May 1996 (17.05.96)	US	9616076.6	31 July 1996 (31.07.96)	GB	9705824.2	20 March 1997 (20.03.97)	GB	(81) Designated States: BR, CA, CN, CZ, HU, JP, MX, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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9705824.2	20 March 1997 (20.03.97)	GB															
(54) Title: DETERGENT COMPOSITION (57) Abstract The invention relates to a detergent composition comprising an anionic and a cationic surfactant, an acid source and an alkaline source capable of reacting together in the presence of water to produce a gas.																	

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Detergent Composition

Technical Field

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The present invention relates to a detergent composition comprising cationic and anionic surfactants and an acid and alkali source, which is suitable for use in laundry washing and dish washing methods.

10

Background to the Invention

There is a trend amongst commercially available granular detergents towards higher bulk densities and towards granular detergent compositions which have a higher content of detergent active ingredients, such as various surfactants. Such detergents offer greater
15 convenience to the consumer. The desire for such concentrated products ensures that the amount of filler materials are reduced and packaging materials which, ultimately, be disposed of.

Amongst consumers there is also a need for detergents which provide improved cleaning
20 and stain removal. Therefore, in the recent past detergents have been developed which contain high levels of surfactant and various types of surfactants, such as anionic, nonionic and cationic surfactants.

The high density detergents, comprising high levels of surfactants can lead to poor
25 solubility properties, arising from low rate of dissolution or the formation of gels, and thus to poor dispensing of the product, either from the dispensing drawer of a washing machine, or from a dosing device placed with the laundry inside the machine. This poor dispensing is often caused by gelling of particles, which have high levels of surfactant, upon contact with water. The gel prevents a proportion of the detergent powder from
30 being solubilized in the wash water which reduces the effectiveness of the powder. This is a particular problem at low water pressures and/or at lower washing temperatures.

WO94/28098 discloses a non-spray-dried detergent powder comprising a combination of
an ethoxylated primary C8-18 alcohol, an alkali metal aluminosilicate builder and 5 to 40
35 wt% of a water-soluble salt of a citric acid.

EP-A-0 639 637 discloses the replacement of perborate bleach with an alkali metal percarbonate to improve the dispensing profile and dissolution rate of a detergent. Citrate or mixtures of citrate with sulphate or carbonate can be used to coat the percarbonate bleach. EP-A-0 639 639 contains a similar disclosure in this respect.

5

The use of effervescence to improve the dispensability of granular materials has been used extensively in pharmaceutical preparations. The most widely used effervescent system in this respect is citric acid in combination with bicarbonate. This effervescent system has also been described for improving the dispersibility of pesticidal compositions for controlling water-borne pests, e.g. GB-A-2,184,946.

10

EP-A-0 534 525 discloses the use of particulate citric acid with a specified particle size range of 350 to 1500 microns.

15 US-A-5, 114,647 discloses a sanitising composition comprising granules of alkali metal carbonate and aliphatic carboxylic acid of a particle size of 150 to 2,000 microns.

EP-A-0 333 223 discloses a bathing preparation comprising fumaric acid having an average particle size of 50-500 microns.

20

The addition of citric acid results in a reduction in alkalinity. However, an alkaline pH is required for an optimum performance of various detergent ingredients, such as certain surfactants. Overall an alkaline pH promotes cleaning, stain removal and soil suspension. Therefore, the incorporation of acids into detergent compositions is undesirable. For example, US-A-4,414,130 discloses detergents, comprising organic acids, wherein certain compounds such as cationic surfactants are preferably omitted.

25

The Applicants now have found that the particular problems associated with dispensing a detergent composition comprising anionic and cationic surfactants can be improved by the inclusion of an acid and an alkali source whilst the performance of the cationic and anionic surfactants is maintained. This eliminates or reduces the problems of solid detergent particles remaining in the washing machine and on washed clothes.

30

Furthermore, since the surfactants are more efficiently dispensed into the wash water, the overall performance of the surfactants is more efficient and an overall improved cleaning, stain removal and soil suspending can be achieved.

35

Furthermore, the detergent residues in the dispensing drawer or dispensing device are reduced.

- 5 All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

- 10 According to the present invention there is provided a detergent composition comprising an anionic surfactant, present at a level of from 0.5% to 60% by weight, a cationic surfactant, present at a level of from 0.01% to 30% by weight, and an acid source and an alkali source wherein said acid source and alkali source are capable of reacting together in the presence of water.

15

Detailed Description of the Invention

20

The detergent composition of the present invention comprises four essential ingredients: anionic surfactant, cationic surfactant, an acid source and an alkali source. These and optional ingredients, and processes for making the detergents, are described in detail below.

25

Detergent Surfactants

The detergent composition can comprise one or more anionic surfactants, as described below, and one or more cationic surfactants.

30

Optionally, additional surfactants, selected from the group consisting of additional anionic and cationic surfactants, nonionic, zwitterionic, ampholytic and amphoteric surfactants can be present.

The total amount of surfactants is preferably of from 1% to 90%, preferably 3% to 70%, more preferably 5% to 40%, even more preferably 10% to 30%, most preferably 12% to 25% by weight of the detergent composition.

- 5 A preferred aspect of the present invention is a granular detergent composition. One or more of the surfactants can be comprised in a base composition, containing preferably also a builder material. The base composition may be prepared by spray-drying and dry-mixing/agglomeration. The base composition may also comprise some or all of the alkali source. Alternatively the acid source and/or alkali source may be added as separate
10 components to the detergent base composition, preferably in a granular form.

Anionic surfactant

- The detergent composition of the present invention comprises one or more anionic
15 surfactants. Any anionic surfactant useful for deterative purposes are suitable. Examples include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

- 20 Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12} - C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6 - C_{14} diesters), N-acyl
25 sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

- The anionic surfactant is present at a level of 0.5% to 60%, preferably at a level of from
30 3% to 50%, more preferably of from 5% to 35%, most preferably from 65 to 20% by weight of the composition.

- The ratio of the anionic surfactant to the cationic surfactant is preferably from 25:1 to 1:3, more preferably from 15:1 to 1:1, most preferably from 10:1 to 1:1.

35

Anionic sulfate surfactant

5 Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

10 Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₉-C₂₂ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

15 Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

20 A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

25 Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

30

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially
5 certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0
10 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)_x-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or
15 unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts
20 of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

25 Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5 - C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1 - C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

30

Cationic surfactant

Another essential component of the detergent composition of the invention is a cationic surfactant, present at a level of from 0.1 % to 30 % by weight of the detergent
35 composition. The cationic surfactant is preferably present at a level of from 0.1 % to

20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3% by weight of the detergent composition.

5 The ratio of the anionic surfactant to the cationic surfactant is preferably from 25:1 to 1:3, more preferably from 15:1 to 1:1, most preferably from 10:1 to 1:1.

10 Preferably the cationic surfactant is selected from the group consisting of cationic ester surfactants, cationic mono-alkoxylated amine surfactants, cationic bis-alkoxylated amine surfactants and mixtures thereof.

Cationic ester surfactant

The cationic surfactant may comprise a cationic ester surfactant.

15 If present in the detergent composition of the invention, the cationic ester surfactant is preferably present at a level from 0.1% to 20.0%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the detergent composition.

20 The cationic ester surfactant is preferably a water dispersible compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

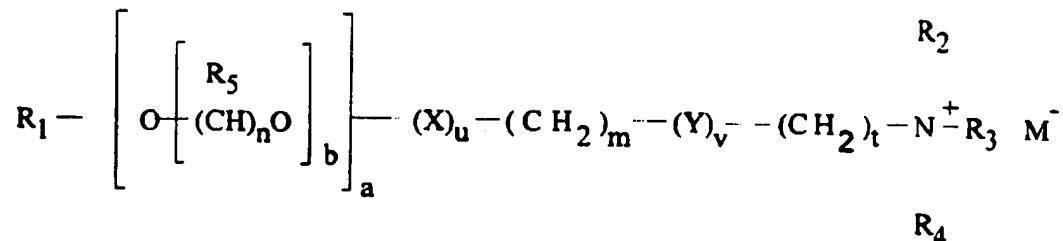
Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

25 In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms.

30 The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain.

Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH₂-O- CH₂- and -CH₂-NH-CH₂- linkages are included. In a preferred aspect the spacer group chain
35 comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

Preferred cationic ester surfactants are those having the formula:

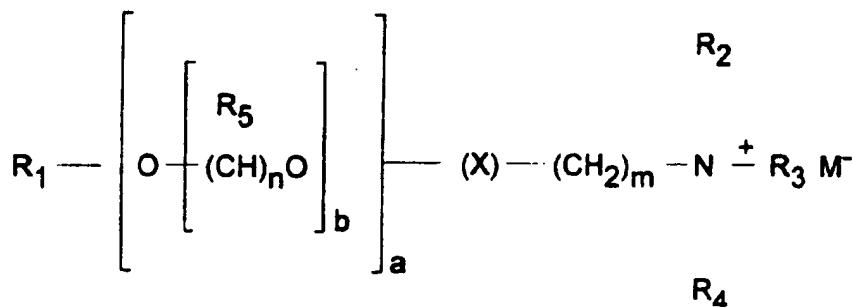


- 5 wherein R_1 is a C_5 - C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^- .
 $N^+(R_6 R_7 R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2 , R_3 , R_4 , R_6 , R_7 , and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1 - C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

15

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

- 20 In a preferred aspect, the cationic ester surfactant is selected from those having the formula:



- 25 wherein R_1 is a C_5 - C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO, OCO, OCOO, OCONH and NHCOO; R_2 , R_3 , and

R_4 are independently selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1 - C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

5

More preferably R_2 , R_3 and R_4 are independently selected from a C_1 - C_4 alkyl group and a C_1 - C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one, of R_2 , R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2 , R_3 and R_4 is a C_2 - C_3 alkyl group, more preferably two C_2 - C_3 alkyl groups are present.

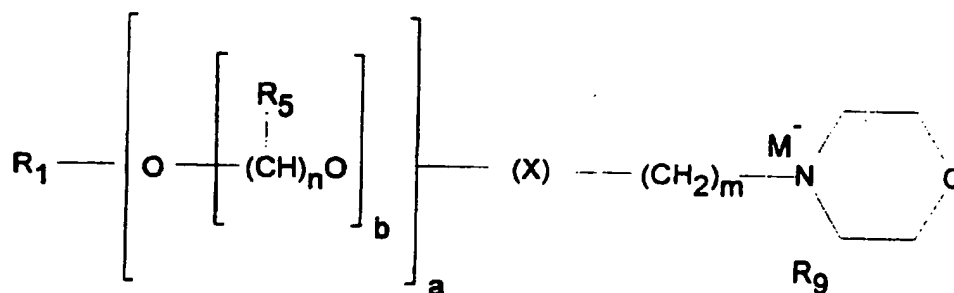
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In a preferred aspect two of R_2 , R_3 and R_4 and the nitrogen of the cationically charged group from part of a ring structure. Preferably, the ring structure contains another nitrogen atom or more preferably, an oxygen atom, or mixtures thereof. Preferably, the ring structure contains 5 to 8 atoms, most preferably 6 atoms.

15

In a highly preferred aspect two of R_2 , R_3 and R_4 and the nitrogen of the cationically charged group from part of a morpholino ring structure or a substituted morpholino ring structure. Highly preferred cationic ester surfactants of this type are the esters having the formula:

20



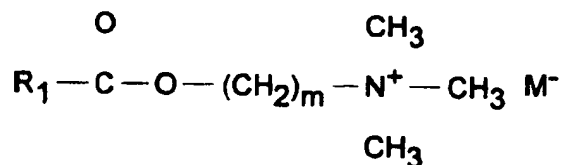
wherein R_1 is a C_5 - C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO , OCO , $OCOO$, $OCONH$ and $NHCOO$; R_9 is selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1 - C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

25

30

More preferably R_2 , R_3 and R_4 are independently selected from a C_1 - C_4 alkyl group and a C_1 - C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one, of R_2 , R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2 , R_3 and R_4 is a C_2 - C_3 alkyl group, more preferably two C_2 - C_3 alkyl groups are present.

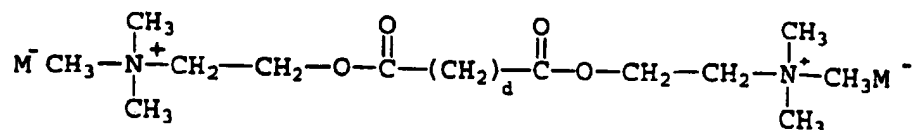
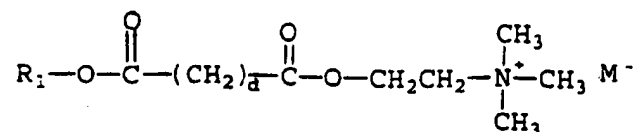
Highly preferred water dispersible cationic ester surfactants are the esters having the formula:



where m is from 1 to 4, preferably 2 or 3 and wherein R_1 is a C_{11} - C_{19} linear or branched alkyl chain.

Particularly preferred choline esters of this type include the stearyl choline ester quaternary methylammonium halides ($R^1 = C_{17}$ alkyl), palmitoyl choline ester quaternary methylammonium halides ($R^1 = C_{15}$ alkyl), myristoyl choline ester quaternary methylammonium halides ($R^1 = C_{13}$ alkyl), lauroyl choline ester methylammonium halides ($R^1 = C_{11}$ alkyl), cocoyl choline ester quaternary methylammonium halides ($R^1 = C_{11}$ - C_{13} alkyl), tallowyl choline ester quaternary methylammonium halides ($R^1 = C_{15}$ - C_{17} alkyl), and any mixtures thereof.

Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.



In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

5

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, water, propylene glycol or preferably a fatty alcohol ethoxylate such as C₁₀-C₁₈ fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

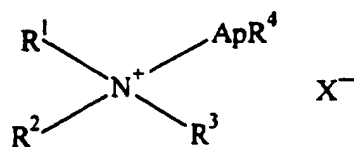
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Cationic mono-alkoxylated amine surfactants

The cationic surfactant of the present invention can contain a cationic mono-alkoxylated amine surfactant, which has the general formula:

20



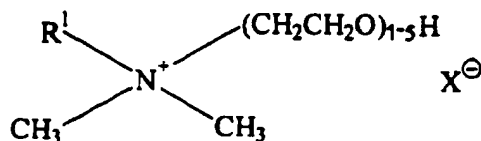
wherein R¹ is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 11 carbon atoms; R² and R³ are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R⁴ is selected from hydrogen

25

(preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C_1 - C_4 alkoxy, especially ethoxy (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; and p is from 1 to about 30, preferably 1 to about 15, most preferably 1 to about 8.

5

Highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



10

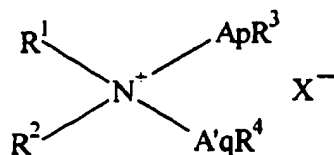
wherein R^1 is C_6 - C_{18} hydrocarbyl and mixtures thereof, preferably C_6 - C_{14} , especially C_6 - C_{11} alkyl, preferably C_8 and C_{10} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

- 15 As noted, compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy, isopropoxy $[CH(CH_3)CH_2O]$ and $[CH_2CH(CH_3)O]$ units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.
- 20 When used in granular detergent compositions cationic mono-alkoxylated amine surfactants wherein the hydrocarbyl substituent R^1 is C_6 - C_{11} , especially C_{10} , are preferred, because they enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials.
- 25 The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention can range from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

Cationic bis-alkoxylated amine surfactant

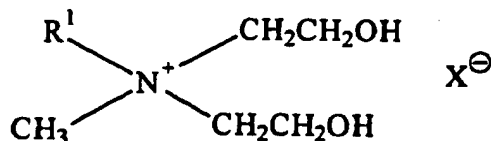
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The cationic surfactant of the invention can be a cationic bis-alkoxylated amine surfactant, which has the general formula:



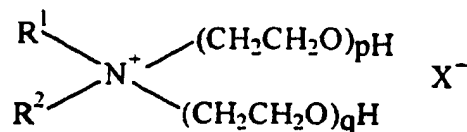
- wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, more preferably 6 to about 11, most preferably from about 8 to about 10 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C_1 - C_4 alkoxy, especially ethoxy, (i.e., $-\text{CH}_2\text{CH}_2\text{O}-$), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

- Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



- wherein R^1 is C_6 - C_{18} hydrocarbyl and mixtures thereof, preferably C_6 , C_8 , C_{10} , C_{12} , C_{14} alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R^1 is derived from (coconut) C_{12} - C_{14} alkyl fraction fatty acids, R^2 is methyl and ApR^3 and A'qR^4 are each monoethoxy.

- Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R¹ is C₆-C₁₈ hydrocarbyl, preferably C₆-C₁₄ alkyl, independently p is 1 to about 3 and q is 1 to about 3, R² is C₁-C₃ alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy (Bu) isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃)O] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

When used in granular detergent compositions in accord with the invention, cationic bisalkoxylated amine surfactants wherein the hydrocarbyl substituent R¹ is C₆-C₁₁, especially C₈ or C₁₀, are preferred cationic surfactants, because they enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials.

The levels of the cationic bis-alkoxylated amine surfactants used in detergent compositions of the invention can range from 0.1 % to 20 %, preferably from 0.4 % to 7 %, most preferably from 0.5 % to about 3.0 %, by weight of the detergent composition.

Alkali Source

In accordance with the present invention, an alkali source is present in the detergent composition such that it has the capacity to react with the source of acidity in the presence of water to produce a gas. Preferably this gas is carbon dioxide, and therefore the alkali is a carbonate, or a suitable derivative thereof.

The detergent composition of the present invention preferably contains from about 2% to about 75%, preferably from about 5% to about 60%, most preferably from about 10% to about 30% by weight of the alkali source. When the alkali source is present in an agglomerated detergent particle, the agglomerate preferably contains from about 10% to about 60% of the alkali source.

In a preferred embodiment, the alkali source is a carbonate. Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate, bicarbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts are also suitable sources of carbonate species and are described in more detail in the section 'inorganic perhydrate salts' herein.

The alkali source may also comprise other components, such as a silicate. Suitable silicates include the water soluble sodium silicates with an SiO_2 : Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2 : Na_2O ratio of 2.0 is the most preferred silicate. Alkali metal persilicates are also suitable sources of silicate herein.

15

Other suitable sources will be known to those skilled in the art.

Acid Source

In accordance with the present invention, the acid source is present in the detergent composition such that it is capable of reacting with the source of alkali in the presence of water to produce a gas.

The acid source is preferably present at a level of from 0.1% to 50%, more preferably from 0.5% to 25%, even more preferably from 1% to 12%, even more preferably from 1% to 7%, most preferably from 2% to 5% by weight of the composition. In a preferred embodiment of the present invention the source of acidity is present in the range of about 1% to about 3%, most preferably about 3% by weight of the composition.

Preferably, 80% or more of the acid source has a particle size in the range of from about 150 microns to about 710 microns, with preferably at least about 37% by weight of the acid source having a particle size of about 350 microns or less. Preferably, 100% of the acid source has a particle size of about 710 microns or less, but this is not essential provided the aforementioned criteria are fulfilled. Alternatively, greater than about 38%, more preferably 38.7%, of the particulate acid source has a particle size of about 350 microns or less.

The particle size of the source of acidity is calculated by sieving a sample of the source of acidity on a series of Tyler sieves. For example, a Tyler seive mesh 100 corresponds to an aperture size of 150 microns. The weight fractions thereby obtained are plotted against the aperture size of the sieves.

The acid source may be any suitable organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. The acid source may be a mono-, bi- or tri-protonic acid. Preferred derivatives include a salt or ester of the acid. The source of acidity is preferably non-hygroscopic, which can improve storage stability. However, a monohydrate acidic source can be useful herein. Organic acids and their derivatives are preferred. The acid is preferably water-soluble. Suitable acids include citric, glutaric, tartaric acid, succinic or adipic acid, monosodium phosphate, sodium hydrogen sulfate, boric acid, or a salt or an ester thereof. Citric acid is especially preferred.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, bleaches, builders, organic polymeric compounds, enzymes, suds suppressers, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Alkoxylated nonionic surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates

with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxyated alcohol surfactant

5

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

15 Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 - C_{19} alkyl or alkenyl, more preferably
20 straight-chain C_9 - C_{17} alkyl or alkenyl, most preferably straight-chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably
25 preferably Z is a glycityl.

Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$
30 wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

35

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

5

Preferred alkylpolyglycosides have the formula



10 wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

15 Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

20 Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group
25 containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} -18 acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc.
30 manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

35 Zwitterionic surfactants can also be incorporated into the detergent compositions or components thereof in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic

secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

- 5 Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂-18 dimethyl-ammonio hexanoate and the C₁₀-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

10

Water-soluble builder compound

- 15 The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

- 20 Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

- 25 The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

- 30 Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the
35 carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands

Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

- Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

- Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

- Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

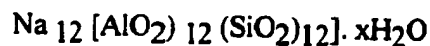
Partially soluble or insoluble builder compound

- The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

- Examples of largely water insoluble builders include the sodium aluminosilicates.

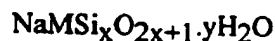
- Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Preferred crystalline layered silicates for use herein have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

Organic peroxyacid bleaching system

A preferred feature of detergent compositions of the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

5

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

10

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

15

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid.

20

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

25 Peroxyacid bleach precursor

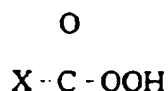
Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as

30

$$\text{O}$$
$$\text{X} - \text{C} - \text{L}$$

where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is

35



- Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

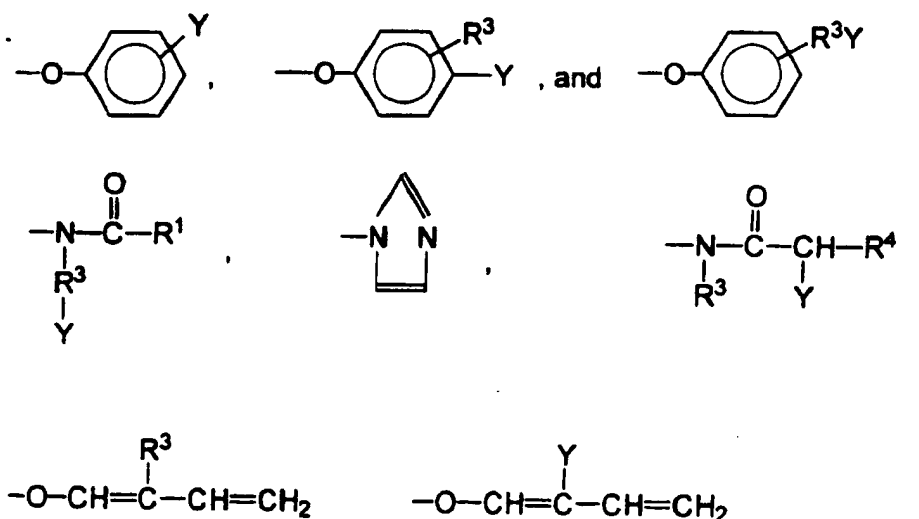
- Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

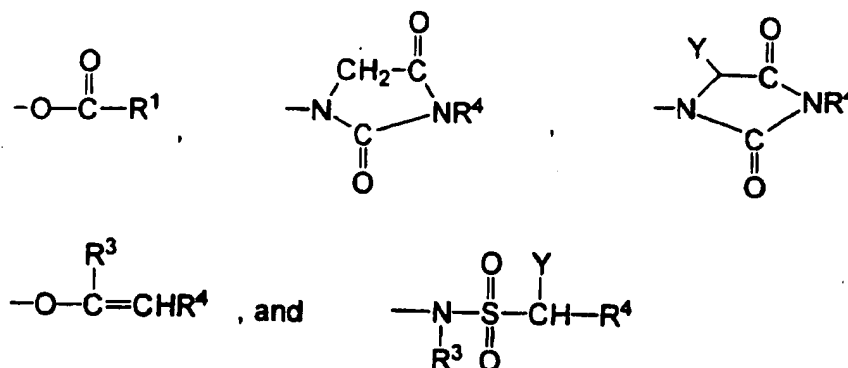
Leaving groups

15

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

- 20 Preferred L groups are selected from the group consisting of:





- and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.
- 10 The preferred solubilizing groups are $\text{---SO}_3^-\text{M}^+$, $\text{---CO}_2^-\text{M}^+$, $\text{---SO}_4^-\text{M}^+$, $\text{---N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O---N(R}^3)_3$ and most preferably $\text{---SO}_3^-\text{M}^+$ and $\text{---CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and
- 15 potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl percarboxylic acid bleach precursors

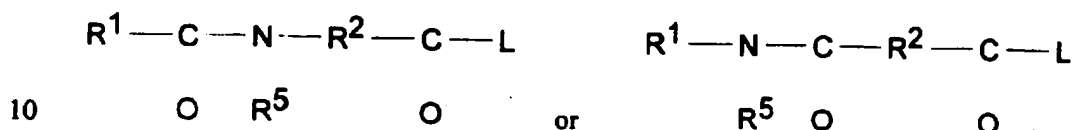
- 20 Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-, N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

5 Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach
 15 activator compounds of this type are described in EP-A-0170386.

20 Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and
 25 unsubstituted benzoyl oxybenzene sulfonates, and the benzylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing
 30 perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

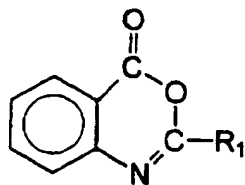
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

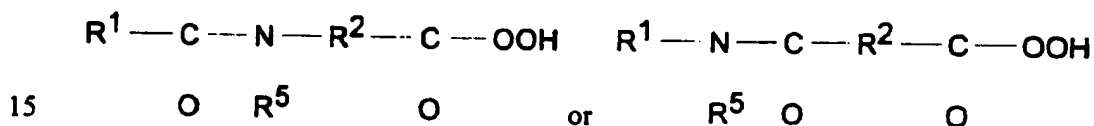


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

5 Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary

metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})(\text{OCH}_3)_3(\text{PF}_6)$. Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

5 The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

10 Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

15 Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy diphosphonates and nitrilo trimethylene phosphonates.

20 Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

25 Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

30 Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

35

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS),
5 ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

10 Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases,
15 lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S
20 (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

25 Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries
30 A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5%
35 by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

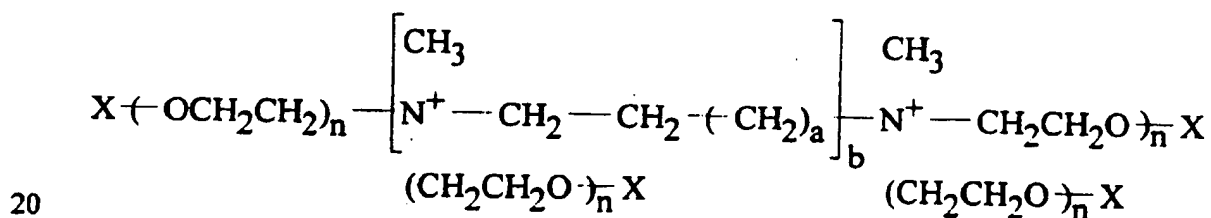
The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

5 Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

10 Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

15 Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



25 wherein X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

30 Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

10

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

15 Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

30 Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkylidiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

35

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a
5 silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to
95% by weight of the silicone antifoam compound; and

10 (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of
the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to
50%, preferably 10% to 40% by weight;

15

(b) a dispersant compound, most preferably comprising a silicone glycol rake
copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to
propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%,
preferably 1% to 10% by weight; a particularly preferred silicone glycol rake
20 copolymer of this type is DCO544, commercially available from DOW Corning
under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈
ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to
25 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and
comprises a silicone antifoam compound and an organic carrier material having a melting
point in the range 50°C to 85°C, wherein the organic carrier material comprises a
30 monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20
carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing
systems wherein the organic carrier material is a fatty acid or alcohol having a carbon
chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of
from 45°C to 80°C.

35

Clay softening system

The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

- 5 The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

10 Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

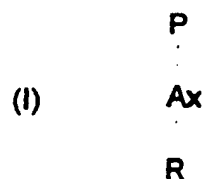
- 15 The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

20

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

25



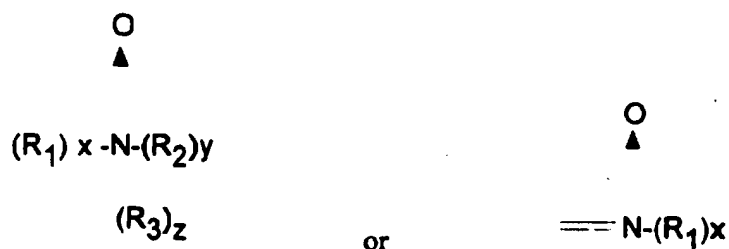
wherein P is a polymerisable unit, and



- 30 A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

- 5 The N-O group can be represented by the following general structures :



- 10 wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

15

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group.

- 20 Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

- 25 Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

30

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-

solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

5

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

10 c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada
15 under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

20

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular
25 weight of from 2,500 to 400,000.

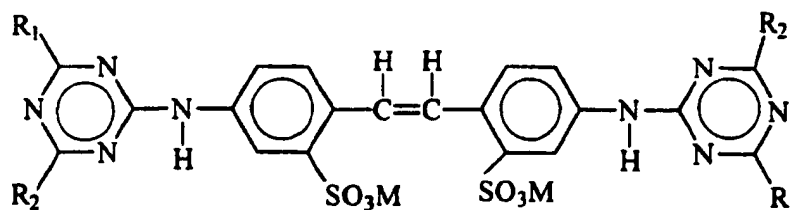
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular
30 weight of from 2,500 to 400,000.

Optical brightener

35 The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



5

wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

- 10 When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener
- 15 useful in the detergent compositions herein.

- When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This
- 20 particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

- When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially
- 25 marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water
5 insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

10

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

15

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 10.0, preferably from 10.0 to 12.5, most preferably from 10.5 to 12.0.

20

Form of the compositions

The detergent composition of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the
25 detergent composition. The acid source of the invention is preferably dry-added.

The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing
30 machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

The mean particle size of the base composition of granular compositions in accordance with the invention can be from 0.1 mm to 5.0 mm, but it should preferably be such that no
35 more that 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves.

5 The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650

10 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower

15 extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap

20 valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

25

Surfactant agglomerate particles

The surfactant system herein is preferably present in granular compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes,

30 noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan

35 agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands.

and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

- 5 A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

10

In an especially preferred embodiment of the present invention, the detergent composition has a density of greater than about 600 g/l and is in the form of powder or a granulate containing more than about 5% by weight of the alkali, preferably (bi-) carbonate or percarbonate. The carbonate material is either dry-added or delivered via agglomerates.

- 15 The addition of the acid, preferably citric acid, (up to 10%) may be introduced into the product as a dry-add, or *via* a separate particle.

Laundry washing method

- 20 Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres,
25 as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

- In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the
30 product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

- Once the washing machine has been loaded with laundry the dispensing device containing
35 the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically

rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

5

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

10

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

15

20

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

30

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective

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material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 5 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

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Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

15

Abbreviations used in following Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

5	LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
	TAS	:	Sodium tallow alkyl sulfate
	C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
	CxyEzS	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z
10			moles of ethylene oxide
	C45E7	:	A C ₁₄ -15 predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
	C25E3	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 3 moles of ethylene oxide
15	C25E5	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 5 moles of ethylene oxide
	CEQ	:	R ₁ COOCH ₂ CH ₂ .N ⁺ (CH ₃) ₃ with R ₁ = C ₁₁ -C ₁₃
	QAS I	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
	QAS II	:	R ₂ .N ⁺ (CH ₃)(C ₂ H ₄ OH) ₂ with R ₂ = C ₁₀ - C ₁₄
20	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
	TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
	TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
25	Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
	NaSKS-6	:	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
30	Citric acid	:	Anhydrous citric acid
	Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
35	Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
	Sodium sulfate	:	Anhydrous sodium sulfate

	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
5	CMC	:	Sodium carboxymethyl cellulose
	Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
10	Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
15	Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
	Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
20	PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
	PB1	:	Anhydrous sodium perborate monohydrate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
25	Percarbonate	:	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
	TAED	:	Tetraacetythylenediamine
30	DTPMP :	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
	Photoactivated	:	Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
35	Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl

	Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
	HEDP	:	1,1-hydroxyethane diphosphonic acid
	PVNO	:	Polyvinylpyridine N-oxide
5	PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
	SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
10	SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
	Silicone antifoam :		Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
15	Alkalinity	:	% weight equivalent of NaOH, as obtained using the alkalinity release test method described herein.

In the following Examples all levels are quoted as % by weight of the composition:

Example 1

5

The following granular laundry detergent compositions A and B of bulk density 750 g/litre were prepared in accord with the invention:

	A	B	C	D
LAS	5.61	4.76	5.5	6.5
TAS	1.86	1.57	2.1	1.5
C45AS	2.24	3.89	2.4	3.2
C25AE3S	0.76	1.18	0.8	1.3
C45E7	-	5.0		2.5
C25E3	5.5	-	2.5	-
CEQ	2.0	1.0	-	-
QAS	-	1.0	2.0	1.5
Zeolite A	19.5	19.5	16.5	16.5
NaSKS-6/citric acid (79:21)	10.6	10.6	10.6	6.9
Carbonate	21.4	21.4	16.5	19.3
Bicarbonate	2.0	2.0	2.0	-
Silicate	2.0	-	-	2.0

Sodium sulfate	-	14.3	-	-
Percarbonate	12.7	-	12.0	-
TAED	3.1	-	4.5	-
DETPMP	0.2	0.2	0.2	0.2
HEDP	0.3	0.3	0.3	0.3
Protease	0.85	0.85	0.85	0.85
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.18
Amylase	0.1	0.1	0.1	0.1
MA/AA	1.6	1.6	1.0	2.2
CMC	0.4	0.4	0.7	0.7
Photoactivated bleach (ppm)	27 ppm	27 ppm	27 ppm	27 ppm
Brightener 1	0.19	0.19	0.19	0.19
Brightener 2	0.04	0.04	0.04	0.04
Perfume	0.3	0.3	0.3	0.3
Silicone antifoam	2.4	2.4	2.4	2.4
Citric acid	1.5	2.0	4.5	5.5
Minors/misc to 100%				

Example 2

The following detergent formulations, according to the present invention were prepared:

	E	F	G
Blown Powder			
STPP	14.0	-	14.0
Zeolite A	-	20.0	-
C45AS	9.0	6.0	8.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	9.0
TAS	2.0	-	-
QAS II	1.5	3.0	3.5
Silicate	7.0	8.0	8.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	26.0	23.0	25.0
Percarbonate	18.0	18.0	10
PB1	-	-	2.0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.25	0.30	0.15
Dry mixed sodium sulfate	3.0	3.0	5.0
Citric acid	2.5	2.0	5.0

Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 3

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

5

	H	I
Blown Powder		
Zeolite A	15.0	-
Sodium sulfate	-	-
LAS	3.0	-
QAS I	-	1.5
CEQ	2.0	1.3
DTPMP	0.4	-
CMC	0.4	-
MA/AA	4.0	-
Agglomerates		
C45AS	-	11.0
LAS	6.0	-
TAS	3.0	-
Silicate	4.0	-
Zeolite A	10.0	13.0
CMC	-	0.5
MA/AA	-	2.0
Carbonate	9.0	7.0
Spray On		
Perfume	0.3	0.5
C45E7	4.0	4.0
C25E3	2.0	2.0
Dry additives		
MA/AA	-	3.0
NaSKS-6	-	12.0
Citric acid	4.0	3.0
Citrate	10.0	8.0
Bicarbonate	7.0	5.0
Carbonate	8.0	7.0

PVPVI/PVNO	0.5	0.5
Alcalase	0.5	0.9
Lipase	0.4	0.4
Amylase	0.6	0.6
Cellulase	0.6	0.6
Silicone antifoam	5.0	5.0
Dry additives		
Sodium sulfate	0.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0
Density (g/litre)	700	700

Example 4

The following detergent formulations, according to the present invention were prepared:

	J	K	L	M
LAS	12.0	12.0	12.0	10.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
QAS II	2.0	1.5	1.0	1.0
STPP	30.0	18.0	15.0	-
Silicate	9.0	7.0	10.0	-
Carbonate	15.0	10.5	15.0	25.0
Bicarbonate	-	10.5	-	-
DTPMP	0.7	1.0	-	-
SRP I	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener I	0.2	0.2	0.08	0.2
percarbonate	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Citric acid	3.5	5.0	3.0	2.0
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 5

The following detergent formulations, according to the present invention were prepared:

	N	O	P
Blown Powder			
Zeolite A	10.0	15.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	10.0	8.0	10.0
C45AS	4.0	5.0	7.0
QAS I	2.0	4.0	1.0
Silicate	-	1.0	7.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	28.0	26.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVL/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
Percarbonate	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Citric acid	2.5	2.5	2.0
Balance (Moisture and Miscellaneous)	100	100	100

Example 6

5 The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	Q	R
Blown Powder		
Zeolite A	15.0	15.0
Sodim sulfate	0.0	0.0
LAS	8.0	3.0
QAS	-	1.5
CEQ	2.0	-
DTPMP	0.4	0.4
CMC	0.4	0.4
MA/AA	4.0	2.0
Agglomerates		
LAS	4.0	4.0
TAS	2.0	1.0
Silicate	3.0	4.0
Zeolite A	8.0	8.0
Carbonate	8.0	6.0
Spray On		
Perfume	0.3	0.3
C45E7	2.0	2.0
C25E3	2.0	-
Dry additives		
Citric acid	2.0	3.0
Citrate	5.0	2.0
Bicarbonate	-	-
Carbonate	8.0	10.0
TAED	6.0	5.0
Percarbonate	14.0	10.0
Polyethylene oxide of MW 5,000,000	-	0.2

Bentonite clay	-	10.0
Protease	1.0	1.0
Lipase	0.4	0.4
Amylase	0.6	0.6
Cellulase	0.6	0.6
Silicone antifoam	5.0	5.0
Dry additives		
Sodium sulfate	2.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0
Density (g/litre)	850	850

Example 7

The following high density detergent formulations, according to the present invention were prepared:

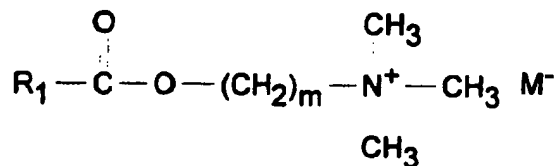
5

	S	T
Agglomerate		
C45AS	11.0	14.0
QAS I	1.0	2.0
CEQ	3.0	-
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C2SE5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
Citric acid	1.5	2.0
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-

Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

WHAT IS CLAIMED IS:

- 1 A detergent composition comprising an anionic surfactant, present at a level of
5 from 0.5% to 60% by weight, a cationic surfactant, present at a level of from 0.01% to
30% by weight, and an acid source and an alkali source wherein said acid source and
alkali source are capable of reacting together in the presence of water.
- 2 A detergent composition according to claim 1 wherein said cationic surfactant is
10 selected from the group consisting of cationic ester surfactants, cationic mono-
alkoxylated amine surfactants, cationic bis-alkoxylated amine surfactants and mixtures
thereof.
3. A detergent composition according to claim 1 or 2 wherein said anionic surfactant
15 is present at a level of from 3% to 50% by weight of the composition.
4. A detergent composition according to any preceding claim wherein said anionic
surfactant is present at a level of from 6% to 20% by weight of the composition.
- 20 5. A detergent composition according to any preceding claim wherein said cationic
surfactant is present at a level of from 0.1% to 20% by weight of the composition.
6. A detergent composition according to any preceding claim wherein the cationic
surfactant is present at a level of from 0.5% to 3% by weight of the composition.
25
7. A detergent composition according to any preceding claim wherein said cationic
ester surfactant is selected from the choline esters having the formula:



30

wherein m is from 1 to 4 and R₁ is a C₁₁-C₁₉ linear or branched alkyl chain.

8. A detergent composition according to any of claims 1 to 5 wherein said cationic
ester surfactant contains a positively charged amine group, substituted with one or two
35 methyl groups and one or two hydroxyethyl or hydroxypropyl groups.

9. A detergent composition according to any preceding claim wherein said cationic mono-alkoxylated amine contains a positively charged amine group, which is substituted with one or two methyl groups, one or two C₆-C₁₈ alkyl groups and one (poly) ethoxy group, with an ethoxylation number of from 1 to 4.
10. A detergent composition according to claim 9 wherein said positively charged amine group is substituted with one or two C₆-C₁₁ alkyl groups.
11. A detergent composition or component thereof according to any preceding claim wherein said cationic bis-ethoxylated amine surfactant contains a positively charged amine group, which is substituted with one methyl group, one C₆-C₁₈ alkyl group and two (poly) ethoxy groups, with each independently an ethoxylation number of from 1 to 4.
12. A detergent composition according to claim 11 wherein said positively charged amine group is substituted with one C₆-C₁₁ alkyl group.
13. A detergent composition or component thereof according to any preceding claim wherein the ratio of anionic surfactant to cationic surfactant is from 25:1 to 1:3.
14. A detergent composition according to any preceding claim wherein the alkali source comprises an alkaline salt selected from an alkali metal or alkaline earth metal carbonate, bicarbonate, sesqui-carbonate, or alkali metal percarbonate salt.
15. A detergent composition according to any preceding claim wherein the acid source comprises an organic, mineral or inorganic acid.
16. A detergent composition according to claim 15 wherein the acid source is glutaric acid, succinic acid, tartaric acid, adipic acid, monosodium phosphate, sodium hydrogen sulfate or boric acid.
17. A detergent composition according to claim 15 wherein the acid source is citric acid.

18. A detergent composition according to any preceding claim wherein the alkali source is present in an amount of from about 2% to about 75% by weight of the composition.
- 5 19. A detergent composition according to any preceding claim wherein the acid source is present in an amount of from 0.5% to 25% by weight of the composition.
20. A detergent composition according to any preceding claim wherein 100% of the acid source has a particle size of no greater than 710 microns.
- 10 21. A method of washing laundry in a domestic washing machine comprising, introducing into a dispensing device which is placed in the drum of the washing machine, or introducing into the dispensing drawer of a washing machine, an effective amount of a detergent composition of any one of claims 1 to 20.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08544

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/62, 3/10, 7/08
US CL : 510/276, 317, 318, 329, 330, 341, 394, 433, 478, 488, 504, 509
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/276, 317, 318, 329, 330, 341, 394, 433, 478, 488, 504, 509

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: choline esters, citric acid, carbonates

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,597,898 A (VANDER MEER) 01 July 1986, col. 5, lines 1-50	1-3
Y	US 4,240,920 A (DE LUQUE) 23 December 1980, col. 8, lines 33-53.	1-3
Y	US 4,321,157 A (HARRIS et al) 23 March 1982, col. 16, lines 1-57.	1-3
Y	US 4,333,862 A (SMITH et al) 08 June 1982, col. 6, lines 10-45.	1-3
Y	US 4,259,217 A (MURPHY) 31 March 1981, col. 13, lines 22-54.	1-3
Y	US 4,220,562 A (SPADINI et al) 02 September 1980 col. 10, lines 5-40.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 07 JULY 1997	Date of mailing of the international search report 24.09.97
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08544

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-21
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.